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NANOPARTICLE-POLYMER COMPLEXATION: ELECTRO-STATIC SELF-ASSEMBLY AS A ROUTE TO STABLE DISPERSIONS OF HYBRID NANOCOLLOIDS

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The inherent instability of inorganic nanoparticle sols may be resolved by complexation with ion-containing polymers at the particle interface. We exploit a precipitation-redispersion (P-R) mechanism to achieve the complexation of short chain polyelectrolytes with cerium oxide nanoparticles in order to extend their stability over a wide pH range. Small-angle x-ray scattering in conjunction with static and dynamic light scattering reveals that P-R may yield hybrid nanocolloidal complexes with a single inorganic core-charged corona structure. The electrostatic self-assembly of ionic stickers anchors the chains onto the surface, resulting in a polymeric brush that provides steric and electrostatic stabilization. This simple strategy to achieve stable dispersions surmounts the critical limitation in the use of nanoparticles, allowing a facile means to translate the intrinsic properties of mineral oxide nanoparticles to a range of novel applications.

Emerging nanomaterials utilize not only the chemical composition but also the size, shape and surface-dependent properties of nanoparticles in applications with remarkable performance characteristics. As synthesized, aqueous dispersions of metal-oxide nanoparticles (e.g. oxides of cerium, iron, or zirconium) exhibit some common properties: *i)* the particles have crystalline structure, *ii)* the sols are typically synthesized in extremely acidic (or basic) conditions, and *iii)* the particles are stabilized by electrostatics and are extremely sensitive to perturbations in pH, ionic strength, and concentration. In order to translate the intrinsic properties of nanoparticles to industrially relevant uses there is a need for a robust means to stabilize nanoparticle dispersions in aqueous media for a variety of processing conditions.

This instability of inorganic nanoparticle sols was resolved by complexation with charged ion-containing polymers. To achieve the goal, we have developed a two-step process, defined as the precipitation-redispersion (P-R) process. In this study we address the issue of the adsorption and of the complexation between cerium

oxide nanoparticles and short poly(acrylic acid) (PAA) chains (molecular weight, $M_w = 2000 \text{ g} \cdot \text{mol}^{-1}$). We demonstrate that we may considerably extend the range of pH and concentration stability of cerium nanosols by irreversibly adsorbing weak polyelectrolytes on the surface. This process does not require mechanical stimulation.

As synthesized, cerium oxide sols at pH 1.4 consist of monodisperse cationic nanocrystalline particles with a hydrodynamic diameter $D_H = 10 \text{ nm}$. Interparticle interactions in the form of strong van der Waals attraction, electrostatic repulsion, and surface chemistry act in concert to make the charged nanosol highly sensitive to the electrostatic environment. Any perturbation in pH (>3) results in aggregation and macroscopic precipitation of the nanoparticle suspension, severely limiting the utility of nanocerium.

Figure 1 shows that when cerium oxide sols are mixed with poly(acrylic acid) solutions (with the same concentration c and pH 1.4), the solution undergoes an instantaneous and macroscopic precipitation. The mixing is characterized by $X_{\text{Mix}} = V_{\text{CeO}_2} / V_{\text{PAA}_{2K}}$, where V_{CeO_2} and $V_{\text{PAA}_{2K}}$ are the respective volumes of the cerium and polymer solutions. Sedimentation or centrifugation gave two distinctly separated phases. Complexation of the polymer chains with several particles results in precipitation due to colloidal bridging, which is reminiscent of classical associative phase separation. As the pH is progressively increased, the suspension spontaneously redisperses into a clear solution. This evolution of the CeO_2 - PAA_{2K} solutions at $X=1$ and $c = 1 \text{ wt. \%}$ is illustrated in **Figure 1A** for the pH range 1.4-10. The precipitation-redis-



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person was followed by static and dynamic light scattering experiments. D_H was found to decrease progressively from 18 nm at pH 7.5 to 12.5 ± 1 nm at pH 10 (**Figure 2B**). This latter value is approximately 3 nm larger than the diameter of the bare particles ($D_H = 9.8$ nm), suggesting that the nanoceria are now coated by a PAA corona.

Figure 2 illustrates the SAXS intensity profiles performed on both bare and PAA_{2K}-coated nanoparticles. At low concentration ($c < 0.5$ wt. % and $X = 1$), where no structure factor is apparent, the scattered intensity is proportional to the concentration and the q -dependence of the intensity reflects the form factor of the aggregates. The form factors for the bare and coated CeO₂-nanoparticles have been shifted vertically so as to superimpose the scattering cross-sections at high wave-vectors (**Figure 2**). This result indicates that on a local scale (*i.e.* below 5 nm) both particles have the same structure. A slight deviation below 0.03 \AA^{-1} is ascribed to the PAA corona surrounding the particles. This is also illustrated in the inset (**Figure 2**) as intensities in a Guinier representation. The logarithm of the intensity decreases linearly with q^2 and from the straight lines we deduce a radius of gyration $R_G = 3.52 \pm 0.02$ nm for the bare particles and $R_G = 4.8 \pm 0.02$ nm for the coated CeO₂-PAA_{2K} particles. As $q \rightarrow 0$, the intensity of the coated particles is 1.4 times that of the bare nanoceria. This value can be used to estimate the number of adsorbed polymers. We assume that a coated nanoparticle is of the core-shell type, having electronic densities ρ_{CeO_2} and ρ_{PAA} . The excess of intensity as $q \rightarrow 0$, due to the PAA shell with respect to that of the bare particles, may

be estimated:

$$\frac{I_{\text{CeO}_2\text{-PAA}}}{I_{\text{CeO}_2}} \bigg|_{q \rightarrow 0} = \left(1 + n_{\text{ads}} \frac{\rho_{\text{PAA}} - \rho_s}{\rho_{\text{CeO}_2} - \rho_s} \frac{V_{\text{PAA}}}{V_{\text{CeO}_2}} \right)^2$$

where ρ_s is the electronic scattering density of the solvent, V_{PAA} is the molar volume of poly(ammonium acrylate) polymer, and V_{CeO_2} is that of the bare particle. We calculate the number of adsorbed polymers $n_{\text{ads}} = 34 \pm 6$. This was corroborated by static light scattering and total organic carbon measurements. The final amount of 40 – 50 polymers per particle corresponds to 1/5 of the total weight of the coated particles.

An insight into the conformation of the adsorbed polymeric corona is obtained. With 50 chains per particle and a monomer molar volume $v_0 = 54.8 \text{ \AA}^3$, the radius of the polymer nanoparticles would be increased by 0.4 nm. With a fully extended polyelectrolyte corona the hybrid nanocolloid would result in $D_H = 18$ nm. With the intermediate redispersed $D_H \sim 13$ nm, the PAA conformation may be described as multisite adsorption of –COOH moieties along the contour length with the remainder constituting a solvated polyelectrolyte brush.

The P-R process is a simple route to obtain single nanoparticles irreversibly coated with PAA chains. With a 2 – 3 nm polyelectrolyte brush surrounding the particles, the cerium sols are stable over a broad range of pH values and concentrations. The process described could easily be extended to other nanoparticle systems. This opens new opportunities with electrostatic self assembly as a means to dramatically improve the stability of inorganic nanosols.

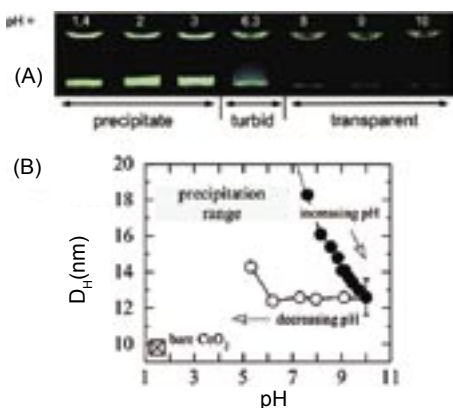


Figure 1. (A) Series of CeO₂-PAA_{2K} solutions prepared at different pH. The mixing of the polymer and cerium solutions was made at pH 1.4, and the pH was further adjusted with NH₄OH. Above pH 7, the precipitate is redispersed. (B) Hydrodynamic diameters measured by dynamic light scattering on CeO₂-PAA_{2K} solutions during the P-R (close symbols). At pH 10, the PAA_{2K}-coated cerium sol is stable and it can be brought back to pH 6 without noticing any change in the dispersion (empty symbols). Below pH 6, the nanoparticles start to aggregate.

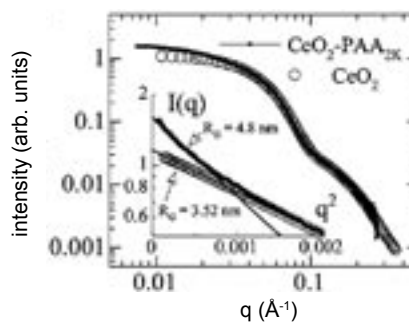


Figure 2. X-ray scattering intensity for bare and PAA_{2K}-coated nanoparticles in double logarithmic scale. The concentrations are in the two cases $c = 0.5$ wt. %. At such low concentrations, the intensities represent the form factors of the particles. The deviation below 0.03 \AA^{-1} is due to the PAA corona surrounding the particles. Inset: Guinier representation of the intensity for the same samples ($I(q)$ versus q^2). From the straight line, the radius of gyration R_G of the nanoceria ($= 3.52 \pm 0.02$ nm) can be calculated.